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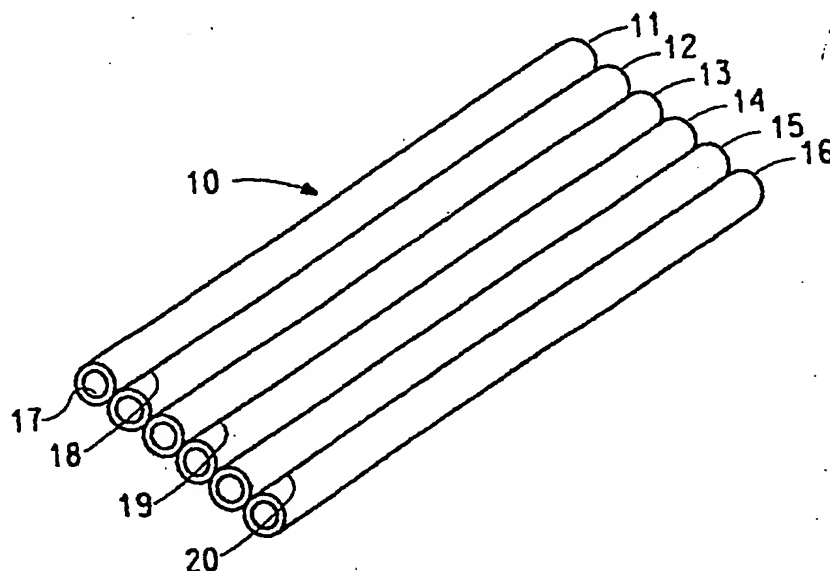
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ning of each regular issue of the PCT Gazette.*

(54) Title: **HEAT EXCHANGER FORMED FROM TUBES JOINED BY SIMULTANEOUS EXTRUSION THERMAL BOND-
ING**



(57) Abstract: Heat exchangers are formed from tubes (11-16) made of polymer, such as nylon. Tube sheets (10) are formed by simultaneous extrusion of tubes (11-16) adhering to each other along their contact line.

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TITLE

HEAT EXCHANGER FORMED FROM TUBES JOINED BY SIMULTANEOUS EXTRUSION THERMAL BONDING

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BACKGROUND OF THE INVENTION

Efficient plate type units (panels) used in nylon heat exchangers are produced by a twin sheet thermoforming process with internal gas assist, which gives an essentially flat plate consisting of a number of tubes joined by ligatures formed from the sheets of nylon. This process is described in US 5,195,240.

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Such plates and the heat exchangers formed from them provide excellent heat transfer efficiency for the space volume occupied, but can tolerate only relatively low internal pressures, restricting their applicability. Tubing formed by extrusion can tolerate much higher internal pressure. In a high efficiency
15 exchanger a large number of small tubes are required; constraint and support of these tubes is required. Use of tubing located between two bonded sheets of plastic to achieve this support is described in US 5,469,915. However, this still requires ligatures between the tubes, which reduces heat transfer efficiency.

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SUMMARY OF THE INVENTION

The present invention provides a heat exchanger made from polymeric tubes in the form of tube sheets with a multiplicity of at least three tubes adjacent each other in a plane, bonded together by extrusion of the tubes.

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BRIEF DESCRIPTION OF THE DRAWINGS

Fig. 1 is a schematic representation of a tube sheet of the invention which has been bonded together by simultaneous extrusion.

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Fig. 2 is a schematic view of an extrusion die that can be used to form the tube sheets or panels of the invention.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

The present invention provides tube sheets or panels constructed from tubes and processes to construct these panels, wherein the tubes are bonded to
35 each other in a parallel, essentially flat manner with no ligature between the tubes. The outer (surface) layer of the tube is a polyamide, preferably nylon 6,6 or modified nylon 6,6. Additional layers of thermoplastic can be incorporated into the tubing by coextrusion to enhance other properties, such as incorporating a

layer of thermotropic liquid crystal polymer (LCP) to enhance the moisture barrier of the structure.

Panel formation is accomplished by simultaneously extruding a
5 multiplicity of tubes in a plane, with the tubes touching each other at the interstices very shortly after exiting the die, allowing tube to tube bonding to take place.

In the drawing, Fig. 1 shows a tube sheet at 10 with tubes 11 – 15 laid adjacent each at 18 – 20. The inside of tubes 11 – 15 shows at 17. The tubes are preferably made of nylon 6,6 or nylon 6 or blends of nylon 6,6 with nylon 6, having an outer diameter of 1 mm to 3.8 mm (0.040 or 0.98 inches). The tubes can be formed by extrusion through a conventional extrusion die shown in Fig. 2 at 30, with die holes 31 – 36 corresponding to tubes 11 – 16. If desired to obtain
15 greater stiffness or greater resistance to permeability, liquid crystal polymers (described below) can be laminated with the nylon 6,6, preferably in a laminate of nylon/LCP/nylon.

In the polymer used in the tubes, other optional ingredients may be
20 selected from flame retardants, anti-blocking agents, slip additives, pigments or dyes, processing aids, plasticizers and ultra-violet blocking agents. These may be used in suitable quantities as are well known to those skilled in the art.

Liquid crystal polymers can also be used in forming layers in the tubes,
25 including: One of the materials which is part of the HESM is an isotropic thermoplastic (ITP). Isotropic herein means that the polymer is isotropic when tested by the TOT Test described in U.S. Patent 4,118,372, which is hereby included by reference. Any ITP may be used so long as it meets certain requirements. It must of course withstand the temperatures to which the HESM is
30 exposed, and should throughout that temperature range provide sufficient strength (together with the LCP) to the HESM to reasonably maintain its shape and contain the fluids in the heat exchanger, as needed. If it is exposed to one or more of the fluids in the heat exchanger (or any other adventitious materials that may contact it) it should be preferably reasonably chemically stable to those fluids so as to
35 maintain its integrity.

Although various types of heat exchangers made simply of ITPs have been described, ITPs sometimes have serious drawbacks when they are the only

materials in HESMs. Sometimes an ITP may not be chemically stable to one or more of the fluids in the heat exchanger, for instance, many polyesters hydrolyze or otherwise degrade in the presence of water, water-alcohol, or water-glycol mixtures, especially at higher than ambient temperatures. Many ITPs are
5 relatively permeable to many liquids and/or gases, and therefore allow losses and/or migration of these materials in or from the heat exchanger. Some ITPs may be swollen by one or more of the fluids used in the heat exchanger thereby changing their dimensions and/or physical properties. All of the above are of course problems in plastic heat exchangers.

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It has been found that a layer of a thermotropic liquid crystalline polymer (LCP) used in the HESM often alleviates or eliminates one or more of the above mentioned problems. By an LCP is meant a polymer that is anisotropic when tested in the TOT Test described in U.S. Patent 4,118,372. If the LCP layer is
15 placed between a fluid and any particular ITP in the HESM it usually protects that ITP from chemical degradation by the fluid, and/or also often protects the ITP from being swollen by that fluid. In addition, even if the ITP is swollen, the LCP because of its high relative stiffness, and the fact that it is not swollen by many fluids, help the overall HESM maintain its shape and dimensions. Also, the LCP
20 acts as an excellent barrier layer to many fluids. For instance, in automotive heat exchangers which help cool the engine, the commonly used internal coolant is a mixture of a glycol and water, and the external coolant is air. With many ITPs diffusion of water and/or glycol is so rapid that frequent replenishment of the water/glycol mixture is needed. If an LCP layer is included, the diffusion is
25 greatly decreased.

In order to obtain rapid heat transfer through the HESM, thickness through the material between the heat transfer fluids should be as small as possible. This would be true with any material used for an HESM, but is especially important
30 with plastics since their heat transfer coefficients are usually relatively low when compared to metals. Since the LCP is usually the more expensive of the polymers present in the HESM, it is economically preferable to limit its use. Therefore, in most constructions it is preferred that the LCP is present in relatively thin layer(s) and that layer(s) of the ITP be relatively thick so as to carry much of the structural
35 load of the HESM (i.e., pressure of the fluid(s), maintain structural shape and dimensions, etc.).

The HESM is made up of one or more LCP layers and one or more layers of ITP. If more than one layer of LCP or ITP is present, more than one type of LCP or ITP, respectively, can be used. In addition other layers may be present. For example, so called tie layers, also called adhesive layers, may be used to increase the adhesion between various LCP and ITP layers, or between ITP layers or between LCP layers. The number and placement of the various layers in the HESM will vary depending on the particular polymers chosen, the fluids used in or by the heat exchanger, temperature requirements, environmental needs, etc.

Most commonly, tie layers and LCP layers will be relatively thin compared to the ITP layer(s). Typical constructions are given below, wherein Fluids 1 and 2 represent the fluids involved in the heat transfer:

- (a) Fluid 1/LCP/ITP/Fluid 2
- (b) Fluid 1/ITP-1/LCP/ITP-2/Fluid 2
- (c) Fluid 1/LCP-1/ITP/LCP-2/Fluid 2
- (d) Fluid 1/ITP-1/LCP-1/ITP-2/LCP-2/Fluid 2
- (e) Fluid 1/ITP-1/ITP-2/LCP/Fluid 2
- (f) Fluid 1/LCP-1/ITP-1/ITP-2/LCP-2/Fluid 2

In all of the above constructions, tie layers may be present between all, some or none of the various polymer layers.

Some of the above constructions may be particularly useful in certain situations. If Fluid 1 but not Fluid 2 chemically attacked the ITP, construction (a) may be particularly useful, but (c) and (f) may also be utilized. If both Fluids 1 and 2 attacked the ITP present construction (c) or (f) may be particularly useful. If one wanted to minimize diffusion of one fluid to another, a construction having two LCP layers, such as (c), (d) or (f) could be chosen. If a special surface is required to reduce abrasive damage on the Fluid 1 side, but great stiffness is also required from the ITP, a construction such as (e) could be chosen wherein ITP-1 and ITP-2 have the requisite properties. These and other combinations of layers having the correct properties for various applications will be obvious to the artisan.

Useful LCPs include those described in U.S. Patents 3,991,013, 3,991,014 4,011,199, 4,048,148, 4,075,262, 4,083,829, 4,118,372, 4,122,070, 4,130,545, 4,153,779, 4,159,365, 4,161,470, 4,169,933, 4,184,996, 4,189,549, 4,219,461,

4,232,143, 4,232,144, 4,245,082, 4,256,624, 4,269,965, 4,272,625, 4,370,466, 4,383,105, 4,447,592, 4,522,974, 4,617,369, 4,664,972, 4,684,712, 4,727,129, 4,727,131, 4,728,714, 4,749,769, 4,762,907, 4,778,927, 4,816,555, 4,849,499, 4,851,496, 4,851,497, 4,857,626, 4,864,013, 4,868,278, 4,882,410, 4,923,947, 5 4,999,416, 5,015,721, 5,015,722, 5,025,082, 5,086,158, 5,102,935, 5,110,896, and 5,143,956, and European Patent Application 356,226. Useful thermotropic LCPs include polyesters, poly(ester-amides), poly(ester-imides), and polyazomethines. Especially useful are LCPs that are polyesters or poly(ester-amides). It is also preferred in these polyesters or poly(ester-amides) that at least about 50 percent, 10 more preferably at least about 75 percent, of the bonds to ester or amide groups, i.e., the free bonds of $-C(O)O-$ and $-C(O)NR^1-$ wherein R^1 is hydrogen or hydrocarbyl, be to carbon atoms which are part of aromatic rings. Included within the definition herein of an LCP is a blend of 2 or more LCPs or a blend of an LCP with one or more ITPs wherein the LCP is the continuous phase.

15 Useful ITPs are those that have the requisite properties as described above, and include: polyolefins such as polyethylene and polypropylene; polyesters such as poly(ethylene terephthalate), poly(butylene terephthalate), poly(ethylene 2,6-naphthalate), and a polyester from 2,2-bis(4-hydroxyphenyl)propane and a 20 combination of isophthalic and terephthalic acids; styrenics such as polystyrene and copolymers of styrene with (meth)acrylic esters; acrylonitrile-butadiene-styrene thermoplastics; (meth)acrylic polymers including homo- and copolymers of the parent acids, and/or their esters and/or amides; polyacetals such as polymethylene oxide; fully and partially fluoropolymers such as 25 polytetrafluoroethylene, polychlorotrifluoroethylene, poly(tetrafluoroethylene/hexafluoropropylene) copolymers, poly[tetrafluoroethylene/perfluoro(propyl vinyl ether)] copolymers, poly(vinyl fluoride), poly(vinylidene fluoride), and poly(vinyl fluoride/ethylene) copolymers; ionomers such as an ionomer of an ethylene-acrylic acid copolymer; 30 polycarbonates; poly(amide-imides); poly(ester-carbonates); poly(imide-ethers); polymethylpentene; linear polyolefins such as polypropylene; poly(etherketoneketone); polyimides; poly(phenylene sulfide); polymers of cyclic olefins; poly(vinylidene chloride); polysulfones; poly(ether-sulfones); and polyamides such as nylon-6,6 nylon-6, nylon-6,12, nylon-6,12, nylon 4,6, and the 35 polyamides from terephthalic acid and/or isophthalic acid and 1,6-hexanediamine and/or 2-methyl-1,5-pentanediamine. Polyamides are preferred ITPs and preferred amides are nylon-6,6, nylon-6, and a copolymer of terephthalic acid with 1,6-hexanediamine and 2-methyl-1,5-pentanediamine wherein 1,6-

hexanediamine is about 30 to about 70 mole percent of the total diamine used to prepare the polymer. Especially preferred polyamides are nylon-6,6, nylon-6 and a copolymer of terephthalic acid with 1,6-hexanediamine and 2-methyl-1,5-pentanediamine wherein 1,6-hexanediamine is about 50 mole percent of the total
5 diamine used to prepare the polymer. Included within the definition of ITP herein are blends of 2 or more ITPs or blends of one or more ITPs with an LCP provided that the ITP(s) is the continuous phase.

One or more (if present) of the ITPs may be toughened. Toughening is
10 known in the art, and may be accomplished by adding one or more or a rubber, functionalized rubber, resin which reacts with the ITP such as an epoxy resin, or other materials. Toughened polyamides are preferred.

The polymers may contain other materials conventionally found in
15 polymers, such as fillers, reinforcing agents, antioxidants, antiozonants, dyes, pigments, etc. An especially useful material is a filler with high heat conductivity, which may increase the efficiency of the heat exchanger.

The composition of a tie layer will depend on which two polymers are on
20 either side of it. For instance the tie layer may be an ITP functionalized or grafted to provide adhesion between the ITP and LCP layers, or may be a blend of one or more ITPs and one or more LCPs.

Typical thicknesses for ITP layers will range from about 0.025 to about
25 0.25 mm. Typical thicknesses for LCP layers will be about 0.01 to about 0.1 mm. Tie layers will usually be as thin as possible, consistent with their providing adhesion between polymer layers. This is usually about 0.01 to about 0.1 mm. The total thickness of the structure is preferably less than about 0.7 mm, more preferably about 0.12 to about 0.5 mm, and especially preferably about 0.15 mm
30 to about 0.4 mm.

Heat exchangers of many different configurations are, made and used, see for instance R. K. Shah, et al., in W. Gerhartz, et al., Ed., Ullmann's Encyclopedia of Industrial Chemistry, 5th Ed., Vol. B-3, VCH Verlagsgesellschaft mbH,
35 Weinheim, 1988, p. 2-1 to 2-108. As can be seen from this article, and is well known in the art, probably the two most common heat exchange "elements" are the tube and the plate. In a tube type heat exchanger one of the fluids flow through a usually circular cross sectioned tube, while the other fluid flows on the

exterior of the tube. Usually many small tubes are employed to create a large heat exchange surface. Sometimes the tubes may be finned for more efficient heat transfer. In a plate element, small passageways, akin to small tubes, are fabricated within a plate of the heat exchange material. One of the fluids flows on the inside of the passageways while the other fluid flows over the exterior surface of the plates. The passageways are usually small to increase surface area, and multiple plates are often used. All of the discussion about heat exchange surface materials also applies to heat exchange panels.

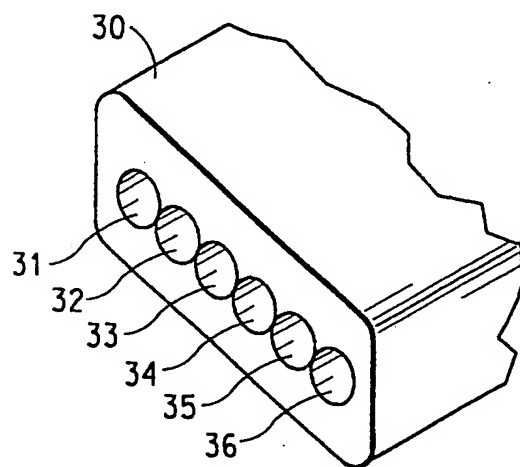
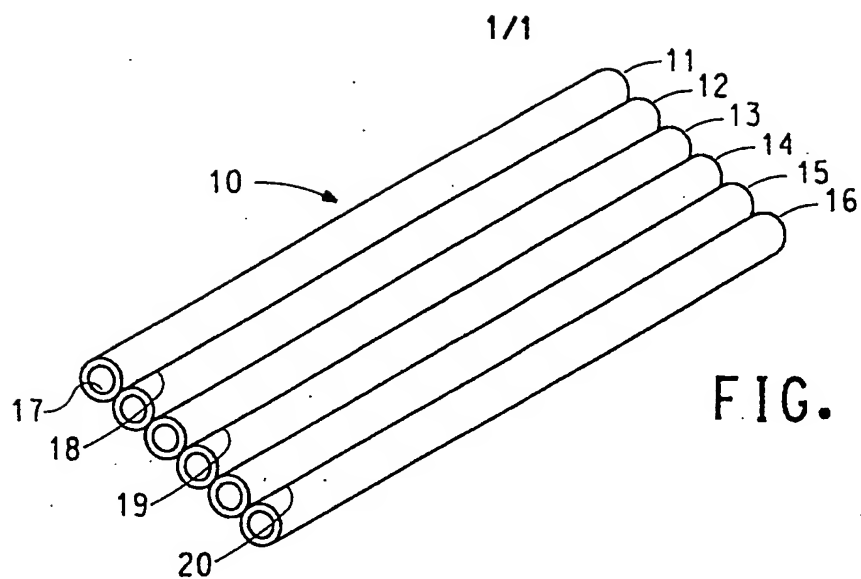
For tube type heat exchangers, the multilayer material described herein can be made by multilayer coextrusion of a tube, see for instance U.S. Patent 5,288,529. However, LCPs when so extruded tend to be weak in the transverse direction (perpendicular to the long axis of the tube). Such problems can be solved by using a counterrotating die for the LCP portion of the extruded tube, as described in U.S. Patents 4,963,428 and 4,966,807, and G.W. Farrell, et al., Journal of Polymer Engineering, vol. 6, p. 263-289 (1986). The tubes can be assembled into a full heat exchanger by inserting them into tanks with proper size holes and sealing the holes with a filler such as epoxy resin, or by heat sealing.

Heat exchanger plates of the layered material described herein may be made by relatively standard methods. They may be directly coextruded, complete with passages in them. A flat sheet or film may be coextruded, thermoformed into the correct shape and joined adhesively or by heat into the plate. Such coextrusions are known processes, see for instance H. Mar, et al., Ed., Encyclopedia of Polymer Science and Engineering, 2nd Ed., Vol. 6, John Wiley & Sons, New York, 1986, p. 608-613, *ibid.*, Vol. 7, 1987, p. 106-127, all of which is hereby included by reference. Individual films or sheets of the ITP(s) and LCP(s) may be laminated together, then formed into a heat exchanger plate. For fabrication of a plastic heat exchanger made with plates see U.S. Patent 4,955,435.

The heat exchangers described herein are useful for automotive and other vehicle uses, in aircraft, as comfort heat exchangers, and various ventilating, heating and air conditioning applications. They are particularly useful as liquid-gas heat exchangers used to cool automotive gasoline or diesel engines. In that case the liquid is water, water and a glycol, or water and an alcohol.

CLAIMS

1. A heat exchanger made from polymeric tubes in the form of tube sheets with a multiplicity of at least three tubes adjacent each other in a plane, bonded together by simultaneously extruding a multiplicity of tubes in a plane.
2. The heat exchanger of claim 1 wherein the tubes are made of polyamide.
3. The heat exchanger of claim 1 wherein at least five tubes are held adjacent each other in a plane.
4. A method for making a tube sheet of claim 3 wherein a multiplicity of tubes held adjacent to each other is provided by simultaneous extrusion of the tubes, so that the outer surfaces adhere to each other.



INTERNATIONAL SEARCH REPORT

International Application No

PCT/CA 00/00739

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	DE 195 29 227 A (STEAG AG) 13 February 1997 (1997-02-13) column 2, line 7 - line 11 column 3, line 11 - line 16; claims 1,2; figure 1	1-4
A	US 3 438 432 A (WETCH JOSEPH R ET AL) 15 April 1969 (1969-04-15) column 3, line 70 -column 4, line 8; figure 4	1-4
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Information on patent family members

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